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XII. *On a new Compound, consisting of Iodide of Potassium, Iodine, and the Essential Oil of Cinnamon.* By JAMES APJOHN, M.D., M.R.I.A., *Professor of Chemistry in the Royal College of Surgeons, Ireland.*

Read 23rd April, 1838.

THE compound which is the subject of the present communication, owes its origin to an unchemical medical prescription. A solution of iodine and iodide of potassium in cinnamon water, having been directed by a physician of this city in the winter of 1837, his patient found that, during the prevalence of very cold weather, the solution, which had been previously turbid, became quite clear, and nearly insipid, and upon examining the bottle closely, he observed deposited in the bottom a small quantity of minute capillary crystals. These crystals were brought to Mr. Moore of Anne-street, the apothecary, in whose establishment the prescription was made up, and by him to me for chemical examination and analysis.

Before detailing the means which I have employed for determining the exact constitution of this substance, it will be proper to give the process by which it is best procured, and enumerate its leading properties; points, both of which were investigated by Mr. Moore and myself conjointly.

To a gallon of cinnamon water,* first reduced nearly to 32°, add four ounces of iodide of potassium and forty grains of iodine, previously dissolved in a minimum of cold water. Upon the instant of admixture the solution becomes quite turbid, owing to the production of a yellowish sediment, and this in less than a minute becomes crystalline, and then gradually subsides. The supernatant solution, which appears almost entirely deprived of iodine and oil of cinnamon, is now drawn off with a syphon, and the crystals and residual fluid thrown upon a single filter, which, when sufficiently drained, is enveloped in several folds of blotting paper, and transferred to a chalk-stone, where by the absorbent powers of the latter, and the occurrence of spontaneous evaporation, the product is rendered perfectly dry and pure. With the quantities stated above sixty grains of the compound are obtained. A temperature at, or very close to 32° is necessary to the success of this process. At 40° the brown powder already noticed is alone produced, and in much diminished quantity. This brown sediment, however, is identical with the crystalline product, for it may be converted into crystals simply by reduction of its temperature ; and I have even found it to undergo the same change when collected on a single filter, and set to dry on a bibulous stone at the temperature of 45°.

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* This water should be prepared by introducing into a still one pound of cassia bark and two gallons of water, and drawing off one gallon.

The crystals are capillary quadrilateral prisms, without pyramidal terminations. They are of a beautiful brown or bronze colour, and have a strong metallic lustre. Their taste is extremely hot and pungent, resembling closely that of oil of cassia, but partaking also of that of iodine. In alcohol and ether they are readily dissolved, and from these solvents they are again deposited with their original appearance upon the occurrence of spontaneous evaporation. They are decomposed by water, which extracts from them iodide of potassium, and causes the separation of oily drops of a dark colour, which are either a mechanical mixture, or a peculiar compound of iodine and the oil of cinnamon. This action of water, however, is greatly diminished when it is close to the freezing point, and appears altogether prevented when a certain amount of iodide of potassium is present.

When heated to 82° the crystals melt into a dark liquid, from which, upon cooling, the original substance is reproduced. When heated beyond its melting point, iodine and a vapour smelling strongly of oil of cinnamon, sublime, and iodide of potassium is left behind, mixed usually with a little carbon, resulting from the decomposition of a portion of the oil. Starch would appear to decompose this substance, for with even its alcoholic or ethereal solution it forms the well-known blue compound. When agitated with water, and zinc or iron filings, an iodide of these metals is produced, and the oil is set free. With mercury the result is the same, and in each instance for water, alcohol or ether may be substituted. Potash also at once developes the oil, forming, as in the case of free iodine, iodide of potassium, and iodate of potash.

From these facts it seems legitimate to infer that it is the oil, and not any modification of it corresponding to the benzoyle of chemists, which is associated with the iodine and iodide of potassium, and that they are all held together by an extremely feeble affinity; inasmuch as not only is the iodide of potassium separated by water, as has been stated, but the iodine is affected by a solution of potash just as if it were free. To test the truth of this opinion, a little of the compound was decomposed in a small glass retort by the exact equivalent of a very dilute caustic alkali, and, a receiver being applied, about half an ounce of a liquid, having the appearance and obvious properties of cinnamon water, was drawn off by distillation. From it, however, I could not, though every precaution was employed, procure a particle of the original crystalline compound. The properties indeed of the distilled liquid were not, upon an accurate examination, identical with those of cinnamon water. Its odour, for example, was slightly different, and it reddened litmus,—a circumstance from which it may be inferred to contain cinnamic acid. It is therefore not unlikely that the oil may have absorbed oxygen, or have been otherwise altered, during the distillation; and as a confirmation of this opinion, I may mention that the oil of cassia which is found in the market abounds in cinnamic acid, and that a cinnamon water prepared from it by a process directed in some of the pharmacopœiæ yields but a very minute proportion of the substance which is the subject of the present paper.

With a view to the analysis of this compound, the first point to determine was the proportion of iodide of potassium which it included. To accomplish this, a known weight of it was heated in a small porcelain capsule, by which iodine and oil of cinnamon were expelled in the vaporous state, and there remained a mixture of iodide of potassium with a little carbon, resulting from the decomposition of a portion of the oil. The iodide of potassium was separated from the carbon by solution in water, and the use of a single filter, which had been previously deprived of all soluble matter by the action, first, of a dilute acid, and subsequently of distilled water. The filter being well washed, the solution was evaporated to dryness in a carefully counterpoised capsule, and then accurately weighed. The following are the results of three experiments thus conducted:

	IK	IK
3.37 grains gave	0.43	12.75 per cent.
8.00 „	1.03	12.87 „
9.40 „	1.13	12.02 „

The mean therefore of the numbers in the third column, or 12.55,* is the quantity of iodide of potassium as obtained by me in 100 grains of the compound.

The next step was to investigate the iodine associated, not with the potassium, but with the oil, and to effect this the following was the course first pursued.

A known weight of the compound was decomposed by a slight excess of an alcoholic solution of potash, and the whole was evaporated to dryness, by which the oil was partly volatilized, and partly decomposed. Heat was now cautiously applied, so as to reduce the iodate, which I have already stated to be always formed in such experiment, to the state of iodide of potassium, but not to volatilize any of the latter salt. The residue, first permitted to cool, was treated with distilled water, and passed through a filter to separate the carbon. The filter was well washed, and the solution, having been reduced to a small bulk by evaporation, was precipitated by nitrate of silver, and the iodide of silver, first edulcorated three or four times with cold distilled water containing a few drops of ammonia, was finally dried, melted, and weighed.

In an experiment in which 10.33 grains of the compound were employed, the iodide of silver amounted to 7.41 grains, equivalent to 3.95 of iodine, or 38.24 for 100 grains of the compound. Now, if from this we subtract 9.58, the iodine in the 12.55 grains of iodide of potassium, which we have already found to exist in 100 of the compound, we will get for the per centage of iodine, in union with the oil, the number 28.66.

Fearing that the heat applied in reducing the iodate of potash to iodide of potassium, might have either been insufficient for the purpose, or have volatilized some of the latter salt, I recommenced the estimation of the amount of free iodine, or rather of that united to the oil, by a somewhat different process.

A known weight of the substance was introduced into a test tube with water and zinc filings, and the other end being drawn out at the spirit lamp, it was hermetically sealed, so as effectually to prevent the volatilization of iodine. Agitation was now resorted to, and a gentle heat at the same time applied, which caused the separation of the oil, the iodine previously combined with it having entered into union with the zinc, and formed with it a salt dissolved by the water. The tube was now broken, and its contents having been thrown upon a single filter previously deprived of all soluble matter, distilled water was poured on until the entire of the iodide of zinc was carried through. The washings were concentrated, suffered to cool, and then treated with the equivalent quantity of nitrate of silver, and the resulting precipitate (iodide of silver) having been, as in the previous experiment, sparingly washed with cold water containing a little ammonia, was dried and weighed. From this the total quantity of iodine in the compound, both that combined with potassium and with the oil, was collected. But the quantity in the former state having been already ascertained, the difference is the iodine associated with the oil.

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* This contains 9.58 grains of iodine.

In an experiment thus conducted 6.55 grains of the substance yielded of iodide of silver 4.52 grains, equivalent to 37.20 grains of iodine for 100 of the compound. Subtracting from this 9.58, the iodine of the iodide of potassium, we obtain, as the representative of the amount of this element associated with the oil, the number 27.62. Hence

$$\frac{28.66+27.62}{2}=28.14$$

is the mean amount of the iodine in the latter state of combination as derivable from both experiments. But

$$\frac{28.14}{9.53}=2.93, \text{ or } q.\,p.=3.$$

We thus arrive at the conclusion, that for every atom of iodide of potassium in the substance under consideration there are three atoms of iodine in combination with the oil of cinnamon.

Before leaving this branch of the analysis I may observe, that the iodine of the oil may be directly obtained by decomposing the compound in a glass tube at a red heat in contact with lime, and acting upon the residue with water, which dissolves the iodide of calcium, and along with it a little lime. The latter being separated in the usual manner by carbonic acid and boiling, the former may be precipitated by oxalate of ammonia, and the iodine estimated from the amount of carbonate of lime afforded by the oxalate when calcined at an obscure red heat. An experiment made upon this plan did not give a very satisfactory result; and, when I considered the great disproportion between the atomic weights of iodine and of lime, I did not feel disposed to repeat the process.

The iodine may also be taken out of the compound by filings of iron, as well as those of zinc, in the form of iodide of this metal; and, though the theoretical objection just stated to the process by lime is equally applicable to this method, a single experiment, whose particulars I subjoin, thus conducted, led to a conclusion corresponding very closely with that already obtained.

Three grains of the compound gave 0.72 of peroxide of iron. But this amount of peroxide corresponds to 2.27 of iodine. Hence 8 : 2.27 : : 100 : 28.41, the per centage of iodine associated with the oil, and which exceeds the result, 28.14, obtained by the other methods, by a quantity so small, that it may be viewed as affording a corroboration of the correctness of the previous determination.

Having determined the iodide of potassium, and the iodine in union with the oil, we can now state the composition of the compound, assuming the residue to be oil of cinnamon.

Iodide of potassium	12.55
Iodine	28.14
Oil of cinnamon	59.30
	99.99

That it is the oil itself, and no oxidized or other modification of it, which exists in this compound, I have already assigned reasons for believing; and as, by the application of such heat as will fuse the compound, no water is set free, it becomes highly probable that the statement above made is a correct representation of its constitution. But the oil of cinnamon has been analyzed, and through the researches of Dumas we are acquainted with its real composition, which he has shown to be represented by the formula $C_{18} H_8 O_2$. If then the view numerically expressed above be the true one, the 59.30 parts of oil must correspond to some integer or at least simple number of atoms. And, reciprocally, if we find such to be the case, we shall be fortified in the conclusion which we have drawn.

With a view to this method of verification, let the numbers which represent the iodide of potassium and iodine, and that which is supposed to represent the oil, be divided by their respective atomic weights, and let the quotients be reduced to others in the same ratio, and so that the iodide of potassium may be represented by unity. When these arithmetical operations are performed, we obtain the numbers in the second and third columns of the following table, the former being the quotients themselves, and the latter other numbers bearing to each other the same proportion.

	(1)	(2)	(3)
Iodide of potassium . .	12.55	0.075	1.000
Iodine	28.14	0.223	2.973
Oil of cinnamon . . .	59.30	0.442	5.893

The numbers, it will be seen, in the last column approximate so clearly to the integers 1, 3, and 6, as to leave little doubt that the true empirical formula is

$$\mathrm{IK} + \mathrm{I}_3 + \mathrm{Cin}_6.\ ^{*}$$

A conclusion which is strikingly confirmed by the following statement of the composition of our substance in 100 parts, calculated upon this hypothesis :

Iodide of potassium	12.26
Iodine	28.08
Oil of cinnamon	59.66
	100.00

To apply, however, to this conclusion the most decisive test, it remained to burn the substance with oxide of copper, and see whether the carbonic acid and water thus obtained would correspond with the amount of oil of cinnamon ascribed to the compound.

7.08 grains (Liebig's apparatus for potash being employed) yielded of carbonic acid 12.70 grains, and of water 2.60,—equivalent to 3.513 carbon, and 0.233 hydrogen. But, adopting for a moment the empirical formula already arrived at, the 7.08 grains of the substance would contain 4.223 of oil of cinnamon. If, therefore, from this we deduct the carbon and hydrogen, we obtain the oxygen, and find the constituents of the oil to be as follows:

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* *Cin* is assumed as the symbol for the oil of cinnamon.

Carbon	3.513
Hydrogen	0.288
Oxygen	0.420

If these be divided by the atomic weights, and that we substitute for the quotients numbers in the same ratio with them, that for carbon being assumed 18, we obtain the following:

Carbon	18.00
Hydrogen	8.82
Oxygen	1.60

As the conjoint result, therefore, of our analysis and our hypothesis, we find the formula for oil of cinnamon to be $C_{18}\ H_{8\cdot82}\ O_{1\cdot60}$. Now this is so close to the formula of Dumas, viz. $C_{18}\ H_8\ O_2$, particularly when we consider that owing to the fusibility of the compound, and the facility with which it is decomposed, heat could not be applied in drying the contents of the tube before the commencement of the combustion, and that consequently the hydrogen must have been too high, and the oxygen too low,—considering this, I say, the accordance is so close as to leave no doubt that the empirical formula already given correctly represents the constitution of the compound submitted to analysis. It is scarcely necessary to say that the most probable rational formula is that here subjoined.

$$IK + 3(I + Cin_2).$$

From the analysis which I first performed, and of which I gave a brief account in the Chemical Section at the Liverpool Meeting of the British Association for the Advancement of Science, the formula deduced was

$$IK + 2(I_2 + Cin_3),$$

which differs from the preceding merely in containing one more atom of iodine.

This compound appears interesting under many points of view. In the first place it is one of considerable complexity, is decomposed with an extreme facility, and is nevertheless perfectly definite in its composition, and even beautifully crystallized.

In the second place it is a kind of double salt, composed of two haloid salts, in one of which the oil performs the very unusual function of an electro-positive or basic metal,—a circumstance the more singular, as Dumas has shown that it unites also to the muriatic and nitric acids, forming with them binary compounds, the latter of which very readily crystallizes. The oil in fact thus appears to act the part of a metal, as well as of an oxide.

Lastly, I may observe that the method by which our compound was first accidentally formed, and is still best made, presents an instance of incompatibility which had not been previously suspected, and will no doubt suggest to chemists experiments which will eventuate in the production of a series of similar substances. In reference, however, to this latter point, I should add, that Mr. Moore has applied to the other aromatic waters the very process which succeeds with cinnamon water, but without obtaining a trace of any new product. It is possible, however, that new results might be obtained by substituting other metals for the potassium, and replacing the iodine by bromine, or even chlorine; and I have indeed myself commenced some experiments with a view to this research.